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ARTICLE TYPE

## Sensitive and selective detection of cesium via fluorescence quenching

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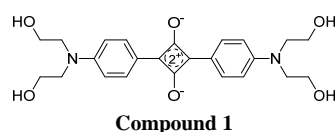
DOI: 10.1039/b000000x

Herein we report a robust and easy method for detecting cesium metal ion ( $\text{Cs}^+$ ) in partially aqueous solutions using the fluorescence quenching of 2,4-bis[4-(*N,N*-dihydroxyethylamino)phenyl]squaraine. This squaraine dye was found to be both highly sensitive (low limits of detection) and selective (limited response to other metals) for cesium ion detection. The detection is likely based on the metal complexing to the dihydroxyethanolamine moieties, which disrupts the donor-acceptor-donor architecture and leads to efficient quenching.

Cesium, which is found in industrial,<sup>1</sup> medical<sup>2</sup> and nuclear wastes,<sup>3</sup> can cause a number of negative health effects, including cardiovascular disease and gastrointestinal distress.<sup>4</sup> Current methods for detecting cesium in complex environments include atomic absorption spectroscopy (AAS),<sup>5</sup> inductively coupled plasma mass spectroscopy (ICP-MS),<sup>6</sup> and solid state sensors.<sup>7</sup> While these methods are highly sensitive and selective for cesium detection, they are often expensive and require sample destruction.

Fluorescence-based methods have rarely been used for cesium detection,<sup>8</sup> even though such methods have the potential to be both cheaper and non-destructive,<sup>9</sup> and have been used successfully for the many analytes.<sup>10</sup> In one example of fluorescence-based cesium detection, researchers synthesized a substituted calixarene that bound cesium with high affinities, resulting in a significant fluorescence enhancement and a 0.3  $\mu\text{M}$  detection limit.<sup>11</sup>

Reported herein is a highly sensitive and selective method for cesium detection that relies on the fluorescence quenching of a near-infrared emitting squaraine fluorophore (compound **1**). Squaraine fluorophores are used extensively in detection schemes due to their narrow absorption and emission bands in the near-infrared spectral region, as well as their marked sensitivity to the surrounding environment.<sup>12</sup> Squaraines have been used to detect metal ions, including mercury, silver, and lead, as well as other transition metals, alkali metals, and lanthanide metals.<sup>13</sup>

Compound **1**

Compound **1** was synthesized following literature-reported

procedures.<sup>14</sup> The fluorescence response of the squaraine to various metal ions was tested by mixing a squaraine solution in DMSO with aqueous solutions of metal ions, and comparing the fluorescence spectra of the resulting solutions with the squaraine fluorescence spectra in the absence of any metal ion (but in the same DMSO-water ratio). The squaraine solution was made fresh daily due to partial degradation under the experimental conditions.

The addition of 1.0 mM of cesium carbonate led to a significant quenching of the squaraine fluorescence to 7.6% of its initial value, as well as a complete disappearance of the characteristic squaraine absorption band (Figure 1). Even as little as 0.010 mM of cesium carbonate caused the squaraine fluorescence to decrease to 92% of its initial value (red line, Figure 1). Plotting this fluorescence quenching as a function of cesium concentration yielded a plot that rapidly approached saturation at high cesium concentrations (Figure 2).

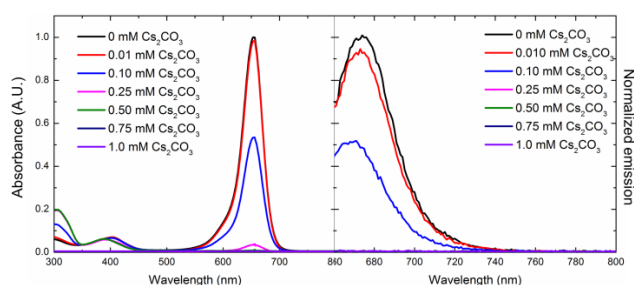


Fig. 1. The absorbance and fluorescence spectra of compound **1** with increasing amounts of cesium carbonate (0.10 mM compound **1**; 650 nm excitation).

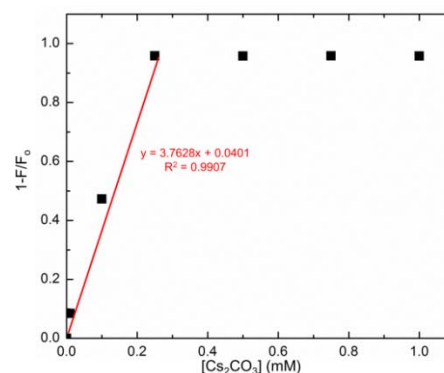


Fig. 2. Illustration of the relationship between cesium concentration and fluorescence quenching.

This complete cesium binding was easily detected by visual inspection of the squaraine solution (Figure 3). The addition of 1.0 mM of cesium carbonate rapidly turned the light blue squaraine solution colorless, whereas other common metal ions displayed no measurable color change.

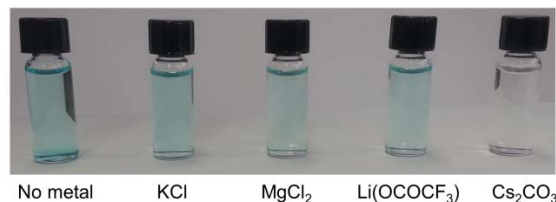


Fig. 3. Visual detection of cesium by color changes of compound 1

The **sensitivity** of this method was determined by calculating the limit of detection. Although this limit is typically defined as three times the standard deviation of the background noise (or ten times the standard deviation for quantification limits),<sup>15</sup> in this case that definition led to a value that was effectively zero. Using 30 times the standard deviation of the background noise for these calculations led to a limit of detection of 0.096  $\mu\text{M}$ , which provides an upper boundary for the detection limit. This detection method is more sensitive than previously reported fluorescence-based methods for purely aqueous solutions,<sup>11</sup> as well as for cesium ion detection in mixed solvent systems.<sup>16</sup>

The **selectivity** of this detection method was determined by screening a wide variety of other metals, including transition metals, alkali metals, and alkali earth metals in a variety of oxidation states. Most of these ions led to no significant changes in the squaraine's fluorescence spectra (Figure 4).

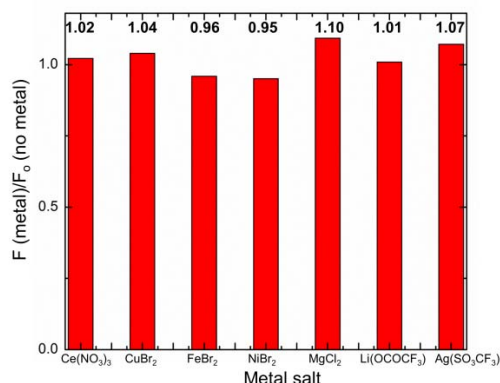


Fig. 4. The effect of metal ion addition on the fluorescence emission spectrum of compound 1 (1.0 mM metal ion; 0.10 mM compound 1).

Preliminary experiments indicate that **both** the carbonate anion and cesium cation are necessary for the highly efficient fluorescence quenching, as no fluorescence quenching was observed for the following species:  $\text{Cs}_2\text{SO}_4$ ,  $\text{CsNO}_3$  and  $\text{CsI}$ . Both  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  induced some degree of squaraine fluorescence quenching, albeit significantly less than the quenching observed for  $\text{Cs}_2\text{CO}_3$  (at 1.0 mM metal ion: 7.6%, 28% and 29% of initial fluorescence was observed for  $\text{Cs}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ , respectively).

The squaraine fluorescence was also partially quenched in the presence of palladium chloride, with the addition of 1.0 mM of palladium chloride leading to a 22% decrease in the squaraine

emission (Figure 5). In this case, the addition of any amount of palladium led to approximately the same degree of fluorescence quenching (17% quenched at  $[\text{PdCl}_2] = 0.010 \text{ mM}$  vs. 22% quenched at  $[\text{PdCl}_2] = 1.0 \text{ mM}$ ), indicating a non-specific fluorescence quenching mechanism.

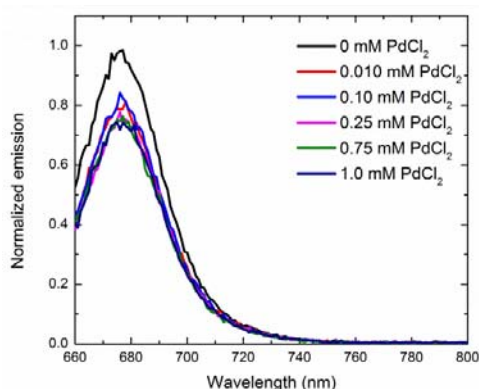


Fig. 5. Partial quenching of compound 1's emission in the presence of palladium (II) chloride

The mechanism of cesium-induced fluorescence quenching is currently under investigation, but the following conclusions can already be drawn: (a) The lack of any bathochromic or hypsochromic shift in the squaraine fluorescence spectra indicates that metal-induced aggregation is unlikely to be a significant contributing factor; (b) the relatively linear relationship between cesium concentration and fluorescence quenching (for low cesium concentrations) indicates that a well-defined ion-squaraine interaction is occurring; and (c) Job plot experiments do not yield a clear stoichiometry between the metal ion and the squaraine fluorophore.

The observed fluorescence quenching is in line with a literature report of a crown-ether containing squaraine whose fluorescence was quenched in the presence of alkali and alkali earth metals.<sup>17</sup> In that report, the authors concluded that the metal ions caused fluorescence quenching through binding in the crown ether moieties, which disrupted the donor-acceptor-donor nature of the squaraine chromophore.<sup>18</sup> Similarly, in this case we expect that the cesium cation binds strongly to diethanolamine, attenuating its strongly donating character and leading to highly efficient fluorescence quenching.<sup>19</sup>

## Conclusions

In conclusion, reported herein is a sensitive and selective method for detecting cesium via fluorescence quenching of a squaraine fluorophore. This detection method has a number of advantages compared to previously-reported systems, including (a) low limits of detection; (b) marked insensitivity to a variety of other common metals; (c) ease of operation; and (d) monitoring of a fluorescent signal in the near-infrared spectral region, which has limited interference from other analytes and will enable detection in complex media. The mechanism of cesium-induced fluorescence quenching and the applicability of this quenching in multiple environments are currently under investigation, and results will be reported in due course.

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## Notes and references

- <sup>5</sup> † Electronic Supplementary Information (ESI) available: Synthesis of compound **1**; detailed procedures for fluorescence quenching experiments and limit of detection experiments, screen of all non-interacting metal ions. See DOI: 10.1039/b000000x/  
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